

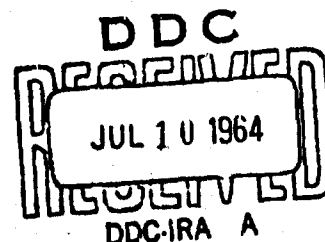
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**FINAL SUMMARY TECHNICAL REPORT
ON THE CALENDAR YEAR 1963
RAMJET TECHNOLOGY PROGRAM**

CONTRACT NO. AF 33(657)-12146

VOLUME 10 OF 12



HIGH TEMPERATURE COATED TUNGSTEN STRUCTURES

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REPORT NO. 25.116



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22

FINAL SUMMARY TECHNICAL REPORT ON THE CALENDAR
YEAR 1963 RAMJET TECHNOLOGY PROGRAM
CONTRACT AF 33(657)-12146

This Report contains a technical summary of all work
accomplished from 25 January 1963 to 31 January 1964.

June 1964

VOLUME 10 OF 12

Prepared By: J. K. Totten
Checked By: J. R. Campbell
Approved By: R. E. Fisher

This Report contains the following section:

SECTION XVIII - HIGH TEMPERATURE COATED TUNGSTEN STRUCTURES

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Report 25,116

FINAL SUMMARY TECHNICAL REPORT ON THE CALENLAR
YEAR 1963 RAMJET TECHNOLOGY PROGRAM

June 1964

VOLUME 10 OF 12

Prepared by:

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FOREWORD

VOLUME 10 OF 12

In accordance with the reporting requirements of Contract AF 33(657)-12146, the following summary technical report is presented. The final report covers all work accomplished from 25 January 1963 through 31 January 1964.

In order to provide a report which can be more easily handled, and to meet the requirements that the materials section be "detachable" and that Proposal Section V be a separable and distinct part, the final summary report has been divided into 12 volumes as follows:

<u>VOLUME</u>	<u>CONTENTS</u>	<u>SECTION NUMBER</u>
1	Electromagnetic Ramjet Research	IV
2	Jet Compressor Research and Ramjet Ejector Investigation	V & VI
3	Extended Mach Number SCRAMJET Investigations	VII
4	Novel Engine Installation Techniques	VIII
5	New and Novel Engine Concepts	X
6	Isotope Ramjet Studies	IX
7	Digital Computer Controls and New Control Studies	XI & XIII
8	Pure Fluid (Non-Moving Part) Control Elements	XII
9	Ramjet Structural Elements, and Non-Regeneratively Cooled Combustion Chambers and Nozzles	XVI & XVII
→ 10	High Temperature Coated Tungsten Structures	XVIII
11	Aerothermal Capability of Plasma Heaters, and High Pressure Air Generation	XIV & XV
12	Extended Mach Number Concepts and Self-Consuming Ramjet Vehicle	XIX & XX

For ease of reading, all figures, tables, and references, have been included within the section with which they are associated. This was accomplished by prefixing all figure, table, and reference numbers with the Roman numeral of their respective section.

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ACKNOWLEDGEMENTS

This report, and the studies and investigations leading to its preparation resulted from the efforts of a large team of engineers and scientists associated with The Marquardt Corporation. Since it would be impractical to list the names of all these persons, only the principal investigators are listed but with acknowledgement intended for all participants.

PROGRAM AREA

High Temperature Coated Tungsten
Structures

PRINCIPAL INVESTIGATORS

K. Marnoch and B. A. Webb

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VAN NUYS, CALIFORNIA

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OBJECT

This report is the Final Summary Technical report on the CY 1963 Ramjet Technology Program and is submitted in partial fulfillment of the reporting requirements as set forth by Contract AF 33(657)-12146. This report presents a technical summary of the work accomplished during the period 25 January 1963 through 31 January 1964.

SUMMARY

The goal of the HIGH TEMPERATURE COATED TUNGSTEN STRUCTURES PROGRAM was to develop methods of protecting tungsten substrates, in oxidizing environments, to temperatures in excess of 3460°R. During the year, material systems of binary, ternary, and quaternary alloys were synthesized in an arc-melting furnace and then screened for oxidation resistance using an oxy-acetylene torch. This resulted in the development of a binary hafnium-tantalum alloy that withstood temperatures well above 3460°R, under oxidizing conditions. The oxide grown from the base alloy was well-bonded, thermal shock resistant, and dense. A feasibility study on the coating of the test specimens was accomplished by plasma-arc spraying and slurry coating the alloy powders onto tungsten and 90 percent tantalum-10 percent tungsten substrates of various configurations. This work has demonstrated the feasibility of utilizing this very promising material system as a coating for oxidation protective refractory metals.

INTRODUCTION

The CY 1963 Ramjet Technology Program was directed toward a comprehensive program of air-breathing propulsion research which was aimed at providing the foundation upon which future engine development programs may be established. This program was slanted strongly toward examination of a number of promising new engine concepts while still providing a well-balanced program of applied research in technological areas related to air-breathing propulsion. This program was an extension and continuation of the Advanced Atmosphere-Breathing Engines and Components Program conducted under the CY 1962 Air Force-Marquardt Contributing Engineering Program, (Contract AF 33(600)-40809).

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XVIII. HIGH TEMPERATURE COATED TUNGSTEN STRUCTURES

Tungsten is the most refractory metal known to date and is of major interest as a high temperature structural material due to its superior strength/weight ratio at elevated temperatures. Prime utilization of tungsten lies in such applications as re-entry cones, leading edges, throat inserts, nozzles etc. on propulsion devices such as solid and liquid fueled rockets, nuclear systems, and ramjets. However, the application of tungsten as a high temperature structural material in oxidizing environments critically depends on protection of the surface from catastrophic oxidation. Oxidation of tungsten in air begins to be appreciable above 1060°R and the rate increases with temperature to about 2260°R. At this point degradation sharply increases due to the volatilization of the tungsten oxide. Concurrent with the volatilization is the internal scaling and contamination associated with diffusion or penetration of oxygen into the metal.

Various coatings have been developed to protect the tungsten from the oxygen attack. Silicide coatings are probably at present the most successful of those developed, particularly the tungsten disilicide. However, as with all silicide base coatings, the temperature limit is about 4060°R or lower and this is approximately the temperature range at which tungsten becomes attractive as a structural substrate.

The most promising means for providing high temperature oxidation protection for tungsten appears to be the formulation of alloys or intermetallic compounds which are refractory, chemically and metallurgically compatible with tungsten and form slow growing, dense and adherent oxides. Such has been the objective of this program: to develop through the study of a number of binary, ternary, and quaternary alloy and intermetallics, a material which oxidizes slowly to form complex oxides capable of protecting tungsten substrates in high temperature oxidizing environments.

A. Analytical Studies

The initial effort on the program was to survey the literature and make a study of thermodynamic and kinetic data on the oxidation of pure metals, alloys, and intermetallic systems. Primarily, an evaluation was made of the thermal stability of the oxidation products of these systems and the characteristics of the simple and complex oxides formed. As ramjet system components are best served by non-ablative materials, the hardware involved under the imposed environmental conditions must be capable of producing a slow growing, adherent, and stable oxide; consequently it is a prime requirement that all of the components of the system should be refractory. This requirement alone severely limited the number of available materials from which a system could be designed. Although the basis of

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the material system for this program (hafnium) was derived analytically, it is quite obvious that the available materials forming very high melting oxides are few. Thoria, hafnia, zirconia and beryllia are actually the only four refractory oxides which presently show sufficient stability to be considered as candidate materials. Of these, thoria is radioactive and beryllia is markedly toxic; therefore, the basis for a system seems likely to be zirconia or hafnia. Of these two, hafnia presents the most attractive properties, particularly from a thermal stability standpoint. The phase transformation of hafnia from monoclinic to tetragonal involves a 3.4 volume percent change versus a 7.5 volume percent change for zirconia. Hafnium also exhibits a higher melting point both as a metal and as an oxide, lower vapor pressure, and a lower diffusion controlled oxidation mechanism than zirconium.

Other oxide forms, however, are not to be discounted. Ceria, yttria, and chromia have proved beneficial as minor additions to materials systems. Yttria, for example, has been found to materially increase the oxidation resistance of many alloy systems.

Since oxidation of the elemental metals and the formation of their respective simple oxides is characterized by excessive oxidation rates, porosity, and breakaway failure modes, it is apparent that the oxides must be modified to provide improved oxidation characteristics. This may be accomplished through fillers such as introducing metals into the oxide of another metal. These additive metals are preferably glass formers or combinations of glass formers. Although the use of a glassy oxide is less than ideal for a protective system due to brittleness, it is, at the present state of coating technology, about the only method of forming a solid (or viscous), inert, and impermeable barrier to oxygen. As with the refractory oxides previously mentioned, there are only about four glass forming oxides which have characteristics applicable to a high temperature coating system: B_2O_3 , SiO_2 , V_2O_5 , and Ta_2O_5 . Of these, B_2O_3 is a low melting glass ($1531^\circ R$) SiO_2 , an intermediate melting glass ($3460^\circ R$), V_2O_5 of questionable properties due to unstable forms, and Ta_2O_5 with probably the highest stable temperature capability ($3910^\circ R$).

Although many investigators have discounted tantalum due to its linear oxidation rate, it is still the most stable high temperature glass forming metal (considering vapor pressure and melting point). From a theoretical standpoint, a protective system developed from the addition of hafnium and tantalum oxides should provide an attractive and basically stable method for protection of substrate material from oxygen contamination. An added bonus in the proposed system is the possibility of growing the desired oxide from a solid solution alloy of the elemental metals.

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However, for the proposed system and many other possible binary, ternary, and quaternary systems, data were unavailable or limited as to the phase relationships, reaction kinetics, thermal stability, thermal expansion, and oxidation behavior. Each of these areas in itself is a major area of study and consequently a method was devised to experimentally screen the materials for applicability.

B. Experimental Investigations

1. Screening

Experimental screening of potential oxidation resistant systems including the hafnium-tantalum alloys was carried out using a technique of arc-melting test buttons and oxidation testing the buttons in an oxy-acetylene torch flame at temperatures greater than 3460°R. The material compositions were prepared by pre-mixing the metal powders, cold compacting the mixture into wafers, and arc-melting the wafers into buttons. By using this method, the arc-melted buttons could conveniently be utilized for metallographic examination, hardness measurements, X-ray diffraction and most important, oxidation resistance screening. Particular care was taken during melting to prevent contamination of the pressed wafers. The melting chamber was usually flushed three times with argon and the melting done at a pressure of about ten inches of mercury. As a further precaution against contamination, a titanium button was melted first to "getter" any possible residual gases in the furnace. These precautions were found particularly necessary with the synthesis of hafnium-tantalum alloys since both of the metals are structure sensitive to embrittlement by elements such as oxygen and nitrogen. Hardness values on the knoop scale increased 40-50 percent for hafnium-tantalum buttons arc melted without a previous titanium melt.

Concurrent with the derivation of the hafnium-tantalum system, arc melted alloys of other potential coating systems were screened by oxidation testing. These systems were based essentially on the refractory metals with alloying additions of silicon, boron, yttrium, lanthanum and chromium. However, the majority of these systems did not show appreciable oxidation resistance. Tested samples either ablated during testing, formed a very thick oxide, or spalled on cooling. One potentially applicable system was developed however, and warranted further evaluation. This was a hafnium based quaternary compound with minor alloying additions of silicon, titanium and yttrium. The alloy stood up well at 4760°R in the oxy-acetylene torch test with a dense, adherent, but fairly thick oxide film. However, further development of this material was postponed due to the derivation of the hafnium-tantalum system with its inherent simplicity as a binary alloy and near term applicability.

In the screening of the hafnium-tantalum system, considerable evaluation was necessary in determining the composition parameters for optimum coating adhesion and oxidation resistance. This evaluation was concerned primarily with the effects of minor or trace amounts of various impurities in the hafnium and tantalum starting powders and the optimum composition of the hafnium-tantalum alloy itself. Tantalum starting powder in the 325-mesh size range was not difficult to obtain in constant high quality lots and within the desired purity specifications. However, hafnium powder that met purity specifications in any size range was difficult to obtain. This is due in large part to the difficulty in separating hafnium from zirconium, the reactivity of hafnium metal itself, and the limited supply through limited usage. To determine more precisely the effect of impurities in the hafnium starting material on the oxidation resistance of the hafnium-tantalum alloy, various grades of hafnium metal powder were procured from several vendors, alloyed with tantalum, and oxidation tested. It was verified that the impurities that were the most difficult to remove from the hafnium powder (Zr, Fe, O₂, N₂) were the ones that most seriously affected the oxidation characteristics of the alloy. Zirconium, although very similar to hafnium, is much more susceptible to oxidation and oxygen diffusion, and consequently forms a much thicker oxide coating under the same test conditions. The formation of iron oxide from greater than 100 ppm of iron impurity reduces the integrity of the oxide coating, leaving it porous and non-adherent. Oxygen and/or nitrogen, in amounts greater than 900-1000 ppm, affected the structure, oxidation kinetics, and physical properties of the base alloy and oxide coat, resulting in a lower temperature capability and greatly reduced oxidation resistance. Unfortunately, hafnium starting material, as supplied by most of the suppliers, had either one or more of the deleterious impurities. Consequently, material with low iron, oxygen, and nitrogen content was chosen as the best available material, considering the profound effects of these impurities on the oxidation characteristics of the Hf-Ta alloy. Zirconium content of the selected hafnium powder was approximately 3 percent.

Typical material specifications for the hafnium and tantalum powder melting stock are shown in Table XVIII-I.

In order to determine the minimum amount of tantalum necessary to provide the optimum oxidation resistance and integrity of the oxide coating, buttons of varying tantalum content were arc melted and oxidation tested. Observed results of these tests are shown in Table XVIII-II.

TABLE XV.11-I

HAFNIUM AND TANTALUM SPECIFICATIONS

<u>Elements</u>	<u>Hafnium Lot #1</u>	<u>Hafnium Lot #2</u>	<u>Hafnium Lot #3</u>	<u>Tantalum Lot #1</u>
Zr	3%	3%	98.6% Hf	-
Fe	77	160	5000	<100
O	830	1500	3500	<1000
N	75	175	55	200
Ta	200	<200	-	99.5%
Cb	<100	150	-	1000
C	50	90	-	50
Cu	<40	<40	80	-
Si	<40	<40	60	300
H	38	80	-	-
Al	25	33	95	<10
Cr	<10	<10	830	-
Mg	<10	<10	600	<10
Mn	<10	<10	130	40
Bi	<10	10	100	-

B, Co, Mo, Pb, Sn, Ti, V, W < 10 ppm each

Analysis in ppm except as noted

TABLE XVIII-II

HAFNIUM-TANTALUM OXIDATION TEST RESULTS

<u>Material</u>	<u>Temperature (Optically Uncorrected)</u>	<u>Time</u>	<u>Observations</u>
Hf-30Ta	4260°R	5 min.	Temperature brought up slowly. Emissivity (transformation) change at 3510°R. Post transformation temperature 3620°R. Momentary bubbling on temperature increase. Glossy white surface.
Hf-20Ta	3910°R	3 min.	Raised slowly to 3910°R, emissivity (transformation) change. Taken to 4260°R. Bubbled for approximately 1 sec., then no change. Surface glossy white.
Hf-15Ta	3940°R	5 min.	No emissivity (transformation) change. Sample gray colored with thin oxide on cool down. (See Figures XVIII-1 & XVIII-2)
Hf-15Ta	4260°R	5 min.	Raised slowly to 4260°R. Emissivity (transformation) occurred at approximately 3960°R. Bubbled momentarily at 4160°R. Surface expanded, porous, and brittle.
Hf-12Ta	4260°R	5 min.	Raised slowly to 4260°R. Emissivity (transformation) change not distinct. Surface spotted with transformed areas.

Hf-151a BUTTON AS ARC MELTED



k-16,468
Reg. 5044-4

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Figure XVIII-1

Hf-151a BUTTON AFTER OXY-ACETYLENE TORCH TEST AT 3940° R
(OPTICALLY UNCORRECTED)



K-16,469
Neg. 5044-5

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Figure XVIII-2

Correlation between the 3940°R test and the 4260°R test on the Hf-15Ta composition is shown in Figure XVIII-3A. The sample at bottom left is as arc melted, that on the right shows the oxide layer of the 3940°R test (Figure XVIII-2), and the upper left shows the 4260°R test and the growth of the porous and brittle outer layer. Figure XVIII-3B shows this transformed area in perspective. Based on the results of these tests the optimum tantalum content appears to lie between 15 and 25 weight percent. Thickness of the oxide coating was essentially the same (10 to 13 mils) on the Hf-30Ta and Hf-15Ta samples. Hf-15Ta samples oxidation tested at 4460°R for ten minutes showed an oxide coating thickness of approximately 20 mils. Although preliminary data have indicated a parabolic oxidation rate for the coating alloy, insufficient tests have been run to firmly establish the oxidation rate as well as the weight change rate.

2. Screening Analysis

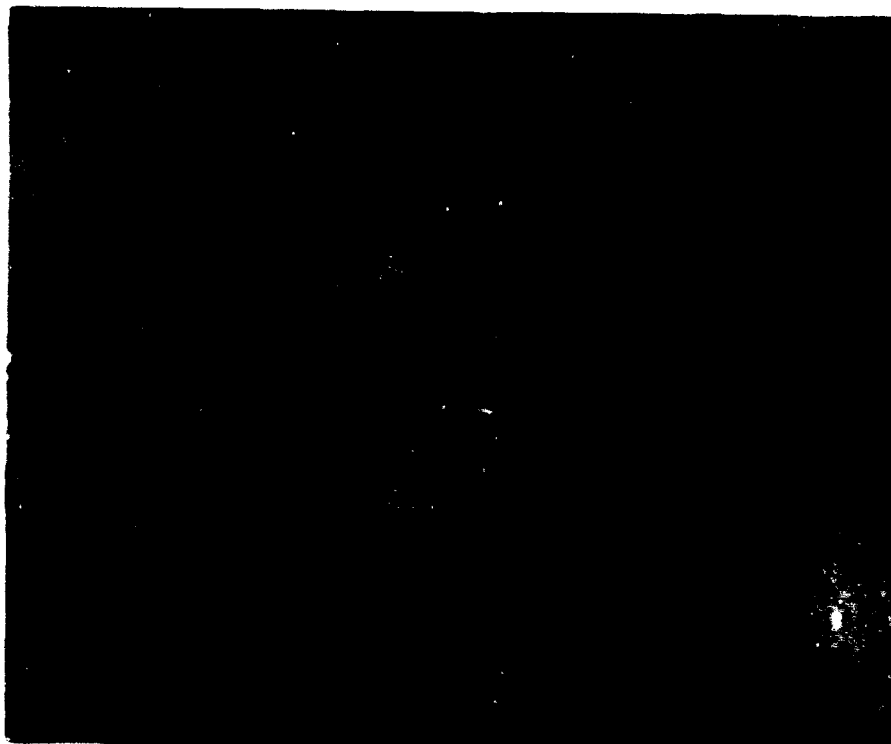
As noted from the previous Hf-15Ta oxidation test data, an emissivity change occurred at approximately 3960°R optical uncorrected (no data have yet been found to indicate the spectral emissivity of hafnia). Literature data have indicated that the transformation temperature of hafnia, grown from the Hf-15Ta buttons, has apparently been stabilized to 3960°R. The volume change and growth of the brittle, porous, and white outer oxide occurs only above this temperature. The gray oxygen deficient sublayer is apparent in all samples and is of about the same thickness regardless of the rate of heating (Figure XVIII-3A). X-ray diffraction analysis of the oxide layers has generally shown the white outer oxide to be equal phases of tetragonal and monoclinic or major phase monoclinic and intermediate phase tetragonal. The lower gray oxide has generally been shown to be major phase tetragonal and intermediate phase monoclinic with the tetragonal crystal structure shifted to a lower "d" value. These X-ray data plus the transformation characteristics suggest stabilization of the high temperature tetragonal hafnia by one or more forms of tantalum oxide, probably TaO₂.

The ability of the oxidation tested buttons to withstand temperatures above the melting point of the alloy is attributed to the low thermal conductivity of the oxide layer (thermal conductivity hafnia - 0.9 Btu/hr-ft-°R at 1960°R, Figure XVIII-4). Samples heated rapidly to 4260-4360°R showed sinking of the blast face indicating melting of the interior. Samples tested to 4560°R and higher (20 to 30 seconds to temperature) withstood the high temperature with no deleterious effects. A reaction zone beneath the oxide layer is believed to be absorbed oxygen (Figure XVIII-5). Hardness profiles from the center outward have shown a hardness increase and embrittlement of the matrix in the reaction zone. Hardness values are similar to those of oxygen contaminated arc melted buttons.

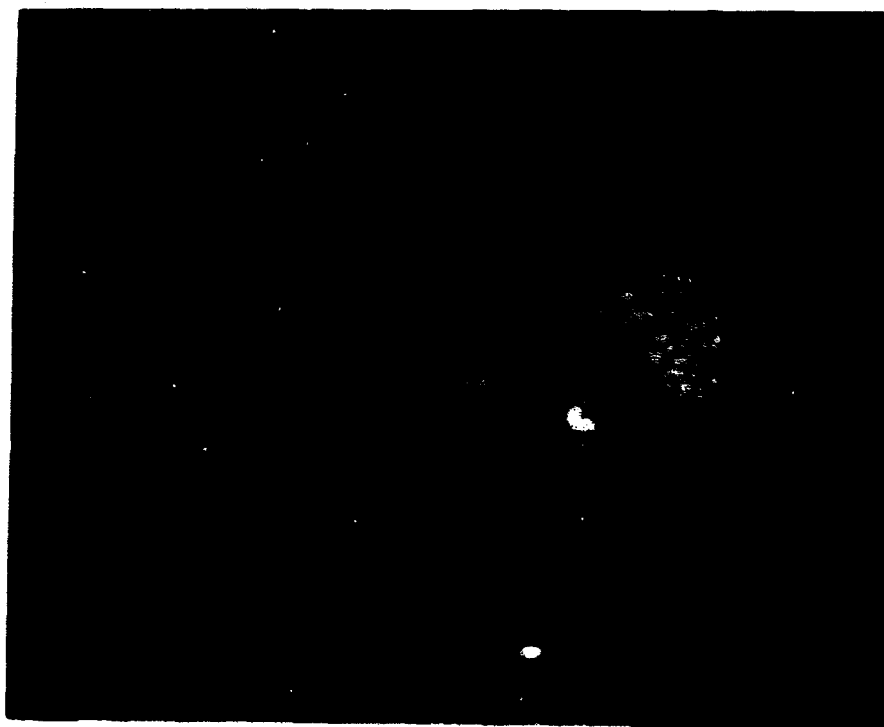
Metallography and X-ray diffraction examination of arc melted buttons has substantiated the eutectic separation indicated by the tentative hafnium-tantalum equilibrium diagram, (Figure XVIII-6). The microstructure is two-phase (major phase hafnium metal and minor tantalum metal) and is very fine, somewhat similar to martensite. The hafnium is oriented about the <103> and <104> reflections.

OXIDATION TESTED Hf-15Ta ALLOY

A.



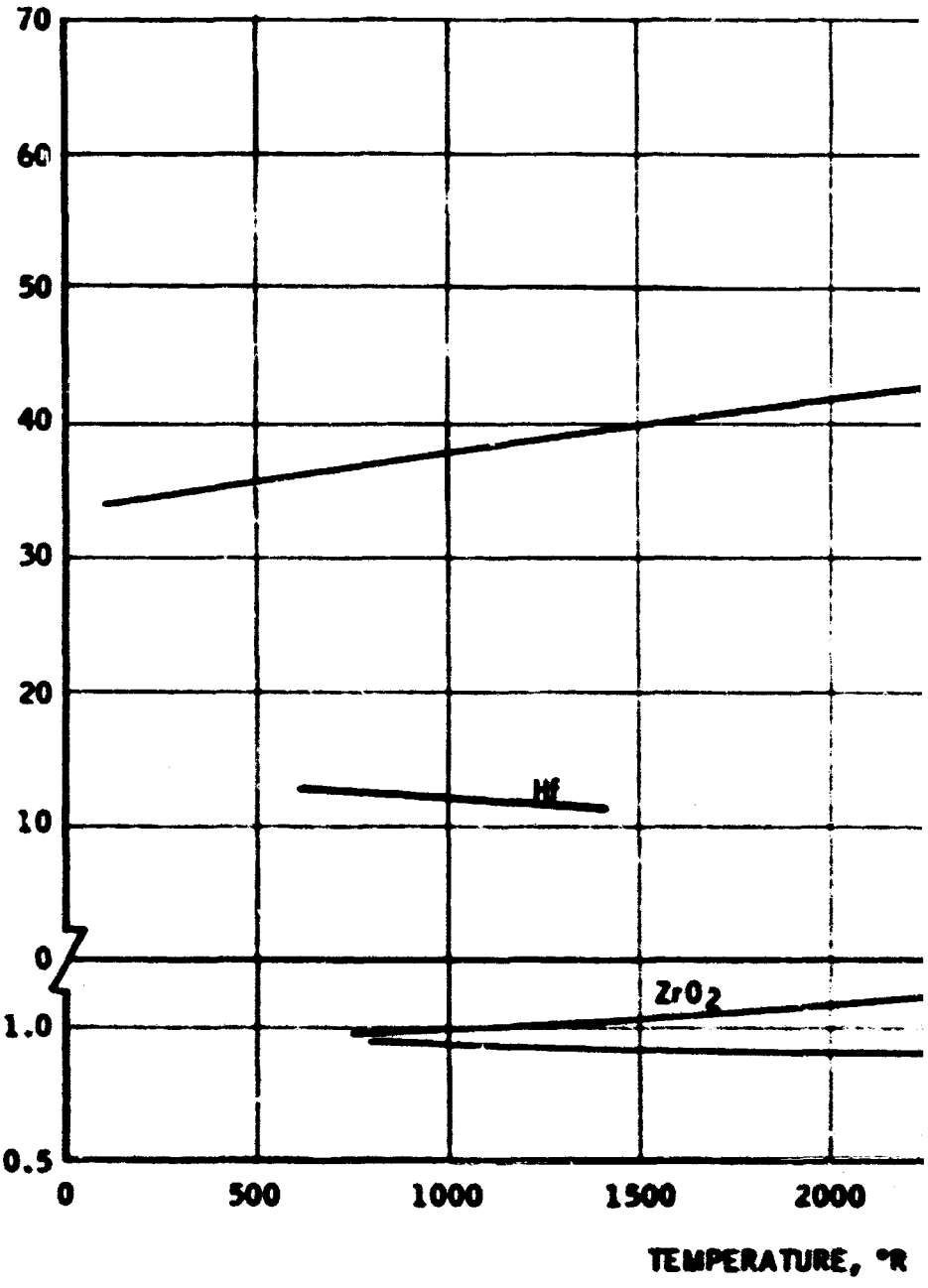
B.



THERMAL CONDUCTIVITY OF SIX

R-16,037

THERMAL CONDUCTIVITY, Btu/hr-ft-°R

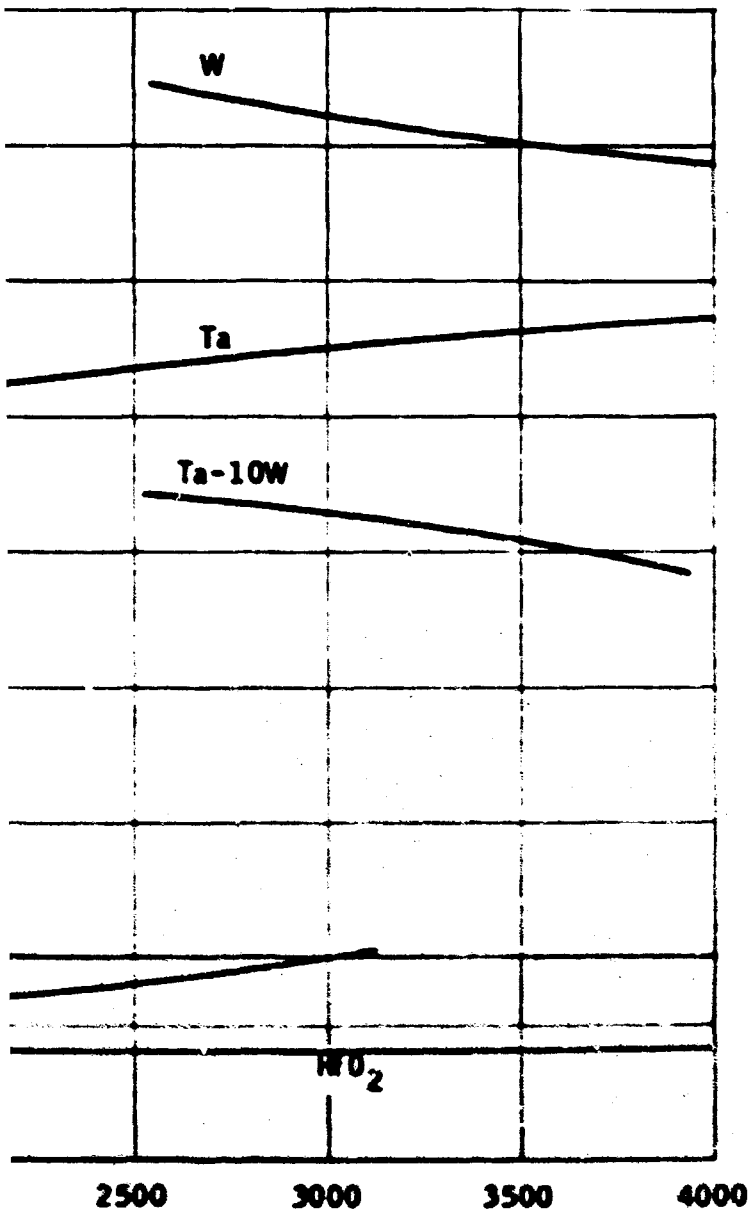


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FIGURE XVIII-4

REFRACTORY MATERIALS



THE
Margardt
INTERNATIONAL
VAN NUYS CALIFORNIA

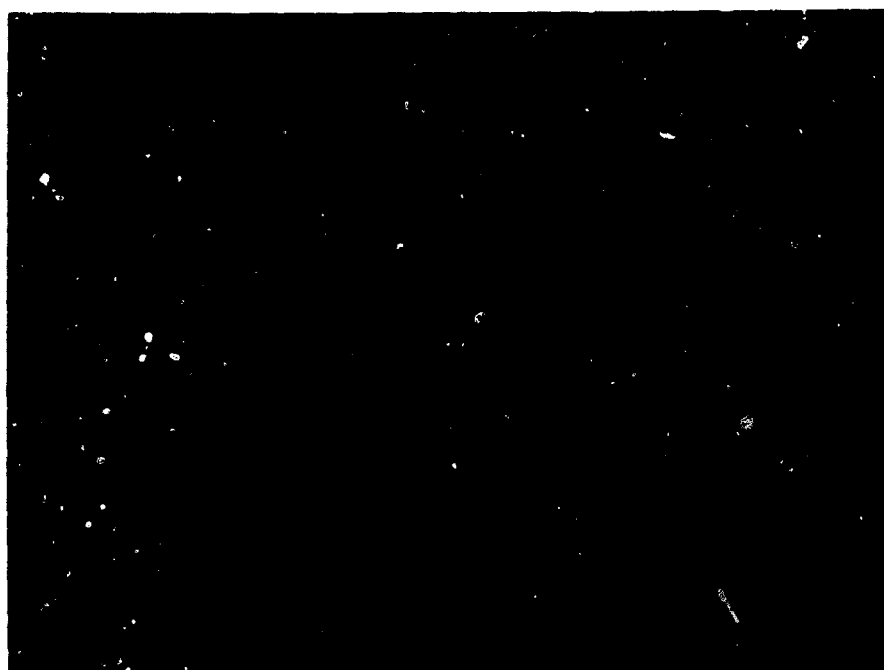
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OXIDATION TESTED Hf-15Ta ALLOY



OXIDE LAYER (600X)

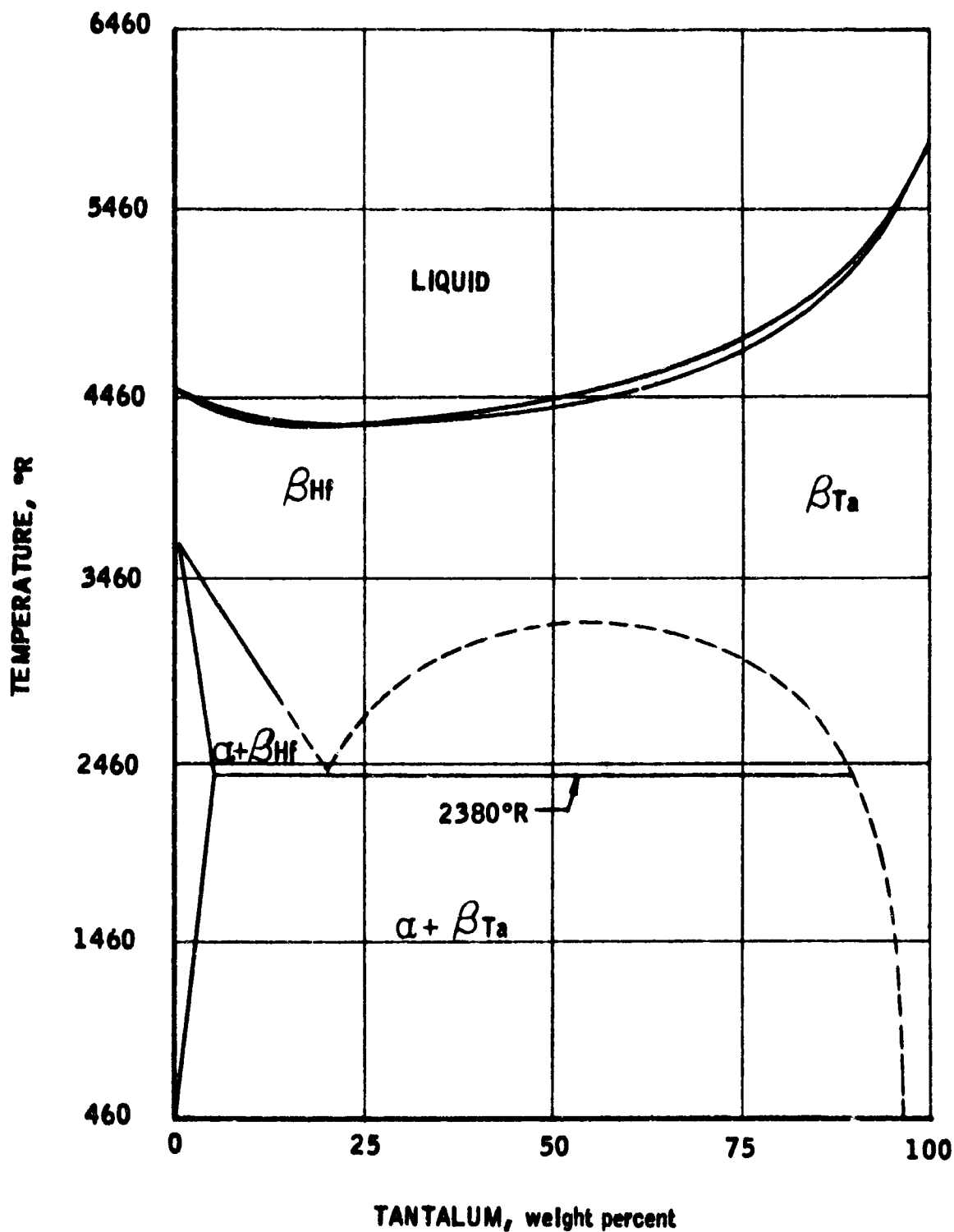


OXIDE LAYER - REACTION ZONE - MATRIX - (150X)

TENTATIVE HAFNIUM-TANTALUM EQUILIBRIUM DIAGRAM

REFERENCE: NUCLEAR FUELS AND MATERIALS DEVELOPMENT

TID-11295, 2nd ED., SEPT. 1962, p. 314



C. Fabrication and Testing

Various techniques for the application of hafnium-tantalum alloys as coatings for tungsten and tungsten alloy substrates were screened for feasibility. The techniques examined were vapor deposition, slurry coating, and plasma-arc spraying.

1. Vapor Deposition

Vapor deposition is a highly promising method for application of coatings because of the high density of the deposited material. Since the life of the Hf-Ta oxidation resistant coating system is essentially dependent on the rate of oxygen permeation through the base alloy as well as the oxide film, the method of application which produces a coating of near theoretical density is desirable. Of the two methods available for vapor deposition of the hafnium-tantalum alloy, hydrogen reduction of the mixed chlorides and thermal reduction of the iodides, the iodide approach appeared the most promising the least complicated. Parameters have been established for the optimum deposition of each metal separately onto 0.010 in. diameter resistance heated wire in a bell jar test apparatus. However, due to the differences in deposition pressure, hafnium deposits best in vacuum and tantalum deposits best at atmospheric pressure - codeposition of the metals is yet to be accomplished.

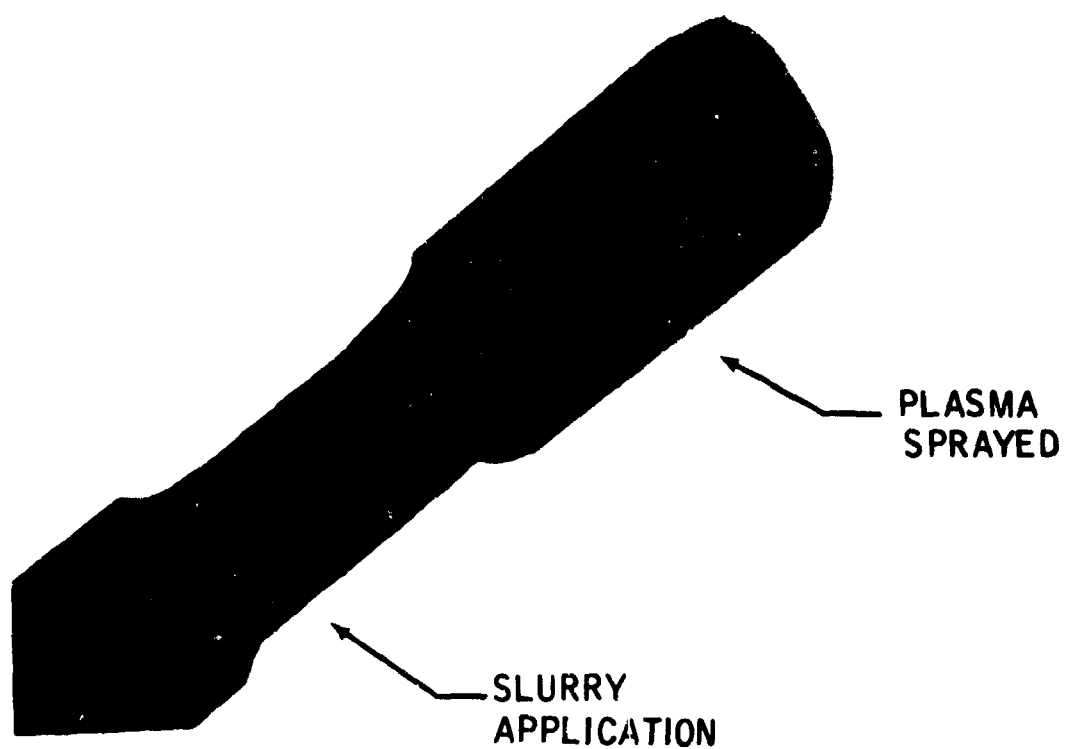
2. Slurry Coating

The preliminary development of a Hf-Ta-Sn slurry has shown promising results. The slurry, a 75 percent Sn powder-25 percent Hf-15Ta powder in a microbrazing-alcohol liquid vehicle was applied to the substrates by both dipping and brushing. The coated specimen was subsequently "cured" by resistance heating to 710-760°R, in vacuum in a bell jar apparatus. Following the curing, the coating was sintered in argon at 2660°R for 45 minutes at a pressure of approximately 20 in. of Hg. The narrow portion of the specimen in Figure XVIII-7 shows the results of oxy-acetylene torch testing for approximately 4½ minutes at 3600°R (optically uncorrected). The upper portion of the specimen was plasma sprayed with Hf-15Ta. Although the coating was not fused and glassy for maximum protection, the tungsten substrate showed no signs of deterioration. Similar results were evident on Ta-10W substrates.

3. Plasma-Arc Spraying

The method of coating application which received the most attention was plasma-arc spraying. This relatively simple and rapid method (due mainly to the simplicity of the binary alloy and applicability to plasma-arc spraying of the mixed powders) promised to provide early utilization of the coating system. An argon carrier cover gas was utilized to preclude oxygen and/or nitrogen contamination of the mixed powders during

Hf-15Ta COATING ON TUNGSTEN SUBSTRATE
OXIDATION TESTED



operation. However, as the operation was carried out in the atmosphere, the sprayed coating analyzed approximately 5-10 percent HfO_2 . To adequately test this method of fabrication, substrate materials of W and Ta-10W of various configurations were plasma-arc coated with approximately 15 mils of Hf-15Ta alloy. The first of the specimens so coated and tested was a Ta-10W tube (Figure XVIII-8A) which was to be used primarily for spectral emittance measurements of hafnium oxide. However, the speckled appearance of the coating at temperature caused by the porosity of the plasma sprayed coating prevented any emittance measurements. The tube did receive a rigorous oxidation test, however; the tube was thermal cycled between room temperature and 1960°R, 2960°R, and 3960°R respectively. Finally, the coated tube was static oxidation tested for 5 minutes at 4060°R (optically uncorrected). Although the oxide contamination of the as-sprayed coating made it far from ideal, post-test metallographic examination showed the coating to be completely oxidized but well bonded to the Ta-10W tube with no spalling evident and minor oxygen penetration into the substrate grain boundaries (Figure XVIII-8B).

A series of test coupons, ½ inch x 3 inch, (Figure XVIII-9A) were plasma sprayed with Hf-15Ta for a coating thickness of approximately 10 mils. Both tungsten and Ta-10W coupons were used. Although only a mechanical bond was achieved on the "as sprayed" specimens, the ductility and ability of the coating to deform with the substrate was evident, particularly with the Ta-10W substrates. The test pieces could be bent through 60 degree arcs 7 to 9 times before separation of the coating and substrate occurred. This ductility was still evident on post-oxidation tested plasma sprayed coupons where the coating would still sustain bends of 45 and 60 degrees. Attempts to sinter the plasma sprayed coating on test coupons met with little success due primarily to the high hafnium oxide content introduced during plasma-arc spraying.

Oxidation testing of the samples was done by the oxy-acetylene torch method and those samples tested "as plasma-sprayed", showed metallurgical bonding of the coating and substrate only at the impingement face of the torch blast. On the reverse side of the coupon, the coating was porous and spalled on deformation. Figure XVIII-9B shows the protection and bonding of the coating on Ta-10W. The oxidation test was for 4½ minutes at 3960°R (optically uncorrected). Figure XVIII-10 shows a plasma-arc sprayed tungsten rod and the subsequent oxidation protection and bonding under similar test parameters. Here also the coating was non-adherent in areas other than the blast face.

Testing of both the slurry coating and plasma sprayed coating under actual service conditions was accomplished under the Non-Regeneratively Cooled Combustion Chamber program (Volume 9 of this report). Utilizing the corrugated combustion chamber concept (Figure XVIII-11) under high temperature and pressure conditions, the ductile hafnium-tantalum coating appeared well suited to match the coating requirements for the Ta-10W chamber.

PLASMA SPRAYED Hf-Ta ALLOY ON Ta-10W

A. Ta-10W TUBE FOR EMITTANCE MEASUREMENTS



**B. OXIDATION TESTED Hf-15Ta COATING ON Ta-10W TUBE
(UNETCHED-600X)**



**OXIDIZED COATING
APPROXIMATELY 0.018 in. THICK**

Ta-10W SUBSTRATE

PLASMA ARC SPRAYED HAFNIUM COATING ON Ta-10W SUBSTRATE

A.



TYPICAL PLASMA ARC SPRAYED COUPON

B.



COATING

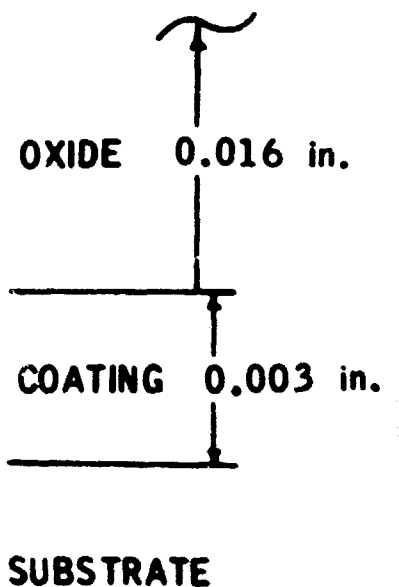
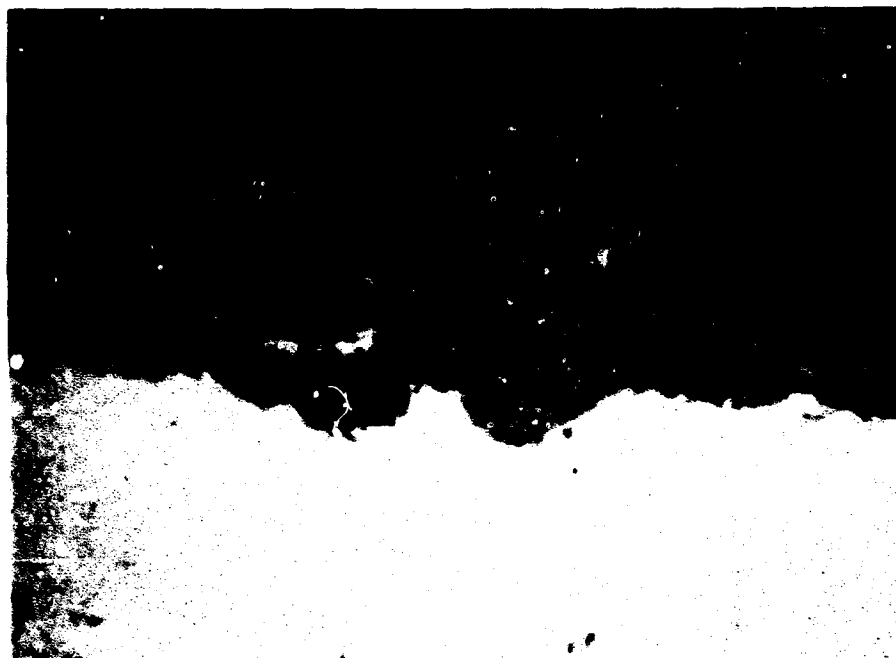
**Ta-10W
SUBSTRATE**

**BONDING AND PROTECTION OF Ta-10W SUBSTRATE
OXIDATION TESTED FOR 4 1/2 MINUTES AT 3960°R
(UNETCHED - 600X)**

PLASMA ARC SPRAYED HAFNIUM COATING ON TUNGSTEN SUBSTRATE



TYPICAL PLASMA ARC SPRAYED TUNGSTEN ROD



BONDING ZONE IN OXIDATION TESTED
Hf-15Ta COATED TUNGSTEN ROD (UNETCHED-600X)

NONREGENERATIVELY COOLED COMBUSTION CHAMBER



R-16,140
Neg. 5081-1

-20-

Figure XVIII-11

Coating of the chamber was accomplished by:

a. Plasma-arc spraying 0.015 inch of Hf-15Ta coating onto the O.D. and 1½ inch in from each end on the I.D. Complete spraying of the I.D. could not be accomplished due to the size of the plasma-arc spray gun.

b. Slurry coating seven inches of the I.D. center with the Hf-Ta-Sn slurry to a thickness of approximately 0.015 inch, curing in an argon atmosphere at 710-760°R to remove the carrier liquid gases, and then sintering at 2460°R for 30 minutes.

The coated chamber was test fired in Marquardt's SUE burner facility utilizing a propane-oxygen fuel mixture. At the onset of test ignition with the chamber, bright sparks were noted in the exhaust gases. These sparks were the result of erosion of the high spots in the slurry coating and consisted of burning particles of coating constituents. After approximately 3-4 minutes of burning at an outside wall temperature of 2310°R, the plasma-arc sprayed coating on the exterior of the cylinder began to spall. After 7 minutes of total burning time the coating had completely spalled off, leaving the Ta-10W substrate exposed to the air. The failure of this sprayed coating essentially resulted because the coating temperature attained was insufficient to provide diffusion bonding and glassing of the coating. The thickness and density of the as-sprayed coating were sufficient to prevent oxygen permeation for 3-4 minutes in a low temperature oxidizing atmosphere. Also, the mechanical bond was of sufficient quality to prevent spalling for the same time and temperature conditions. Following a general rule that 70 to 80 percent of the melting temperature of one of the constituent metals must be reached to provide the activation for diffusion bonding, a temperature of 3460°R was necessary for any activation of the hafnium metal in the coatings. To implement glassing of the tantalum phase to prevent oxygen permeation and densification of the coating, a temperature of 2960-3060°R was necessary. However, even 2960°R was not reached rapidly enough and the coating failed by oxygen contamination of the coating-substrate interface and the spalling subsequently occurred.

A post firing cross-section analysis of the cylinder showed the outside diameter of the crest to be covered with a white 10 mil scale of the low temperature stable β Ta_2O_5 . Under this was 30 mils of oxygen contaminated substrate (Ta will absorb 30 volumes of O_2 before forming an oxide) and finally at the inside of the chamber a 30-40 mil oxide of β Ta_2O_5 , TaO_x and TaO_y . The roots of the cylinder, hotter than the crests and more exposed to erosion, were completely oxidized. A thin scale on the inside of the crests was shown by X-ray analysis to be β Ta_2O_5 , HfO_2 , and α Ta_2O_5 , a high temperature stable form of Ta_2O_5 apparently

stabilized by the HfO_2 . Although this evidence shows some coating remaining on the inside, it was not sufficient to prevent oxidation of the underlying Ta-10W substrate. A photo of the tested cylinder following 15 minutes test time is shown in Figure XVIII-12. The ultimate failure mode consisted of a blow out of one section of the chamber crest.

D. Conclusions and Recommendations

The primary objective of this program, the development and evaluation of a protective system capable of providing high temperature oxidation resistance for tungsten structural components, has been achieved from a sound theoretical basis. The development of the Hf-Ta binary system is a unique advancement in the high temperature (above 3460°R) oxidation protection of refractory substrates such as tungsten and Ta-10W. Since the development of the hafnium-tantalum alloy is a new concept in coating technology, a major portion of the initial development has necessarily been spent in determining and understanding the basic metallurgical, chemical, and physical properties of the alloy. Consequently, through screening and oxidation testing of arc melted buttons and preliminary fabrication and oxidation testing of coated specimens, primarily the feasibility of the coating material has been established.

Studies of the basic hafnium-tantalum alloy show:

1. The material is ductile as compared to the brittle nature of most coating materials.
2. Impurities of Fe, N_2 , and O_2 detract from the ductility and oxidation resistance.
3. Oxidation of the alloy produces an oxide coating which is well bonded and shock resistant. An oxide coating thickness of approximately 0.020 inch is produced after 10 minutes at 4460°R in an oxy-acetylene torch flame.
4. The dense, high temperature stable form of hafnium oxide is apparently stabilized to room temperature by tantalum oxide. Oxidation resistance and integrity of the oxide coating is dependent on this dense form of hafnium oxide.

Evaluation of the application of the alloy as a coating shows:

1. Qualified plasma sprayed and slurry coatings have been applied to tungsten and tantalum-10 tungsten substrates. These coatings must be qualified due to their preliminary nature and the integrity of the coatings produced.

NONREGENERATIVELY COOLED COMBUSTION CHAMBER

AFTER TEST



R-10,141
Neg. T3145-11

Figure XVIII-12